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Multiple twinning on a silica mesoporous crystal

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シリカメソ多孔結晶は、アモルファスシリカを骨格にメソスケールの空隙（2 – 50 nm）が周期配列した結晶である。シリカメソ多孔結晶は、シリカの前駆体と水における界面活性剤の共同的な自己組織化を利用して合成され、界面活性剤は焼成によって取り除かれる。従ってその空隙は水-界面活性剤-シリカ系での界面活性剤ミセルの構造を反映すると考えられる。本研究で我々は十面体や二十面体のような結晶学的点群とは相容れない粒子外形を示すシリカメソ多孔結晶の構造解析を行った。まず電子線結晶学に基づいた高分解能電子顕微鏡像の解析から、その結晶構造は球状ミセルの立方最密充填であることを示す。また特徴的な上記結晶外形はメソスケールにおける多重双晶の結果であることを報告する。

Silica mesoporous crystals[1] are structurally characteristic because of the disordering on the atomic scale and the ordering on the mesoscopic scale, where mesoscopic pores (2 – 50 nm) are periodically arranged. Syntheses of silica mesoporous crystals are generally based on a self-assembly of surfactants and silica precursors in the presence of water. Through the calcination process to remove surfactants, spaces occupied by surfactants are replaced with pores. Therefore, a structure of a silica mesoporous crystal can be interpreted as the “frozen” version of the structure build by micelles composed of surfactants.

In this study, a structural analysis of a silica mesoporous crystal, which exhibited peculiar morphologies such as icosahedral and decahedral shapes, was performed by powder XRD, both scanning and transmission electron microscopes. Through the electron crystallographic analysis[2] on the high resolution electron micrographs, the three-dimensional (3D) electrostatic potential distribution was obtained. The structural solution of this crystal was determined to be the cubic closest packing of spherical pores with the space group symmetry of $Fm\bar{3}m$, as shown in Figure 1.

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Peculiar morphologies of an icosahedron and a decahedron were elucidated on the basis of the multiply twinned particle (MTP) model[3], as shown in Figure 2 and 3. Nowadays, the occurrence of MTP is common in face-centred cubic metal nanoparticles with atomistic constituents such as Au, Ag, Pt, etc. When replacing such atomistic constituents with spherical micelles, morphologies observed are interpreted as MTPs occurring on the mesoscopic scale, which gives rise to the five-fold symmetry as well as quasi-crystals.

We discuss MTPs of the mesostructure[4] in lights of the synthesis condition, spherical micelles and their closest packings. The particle size dependence on the morphology is also discussed in terms of the internal strain introduced during the growth process.

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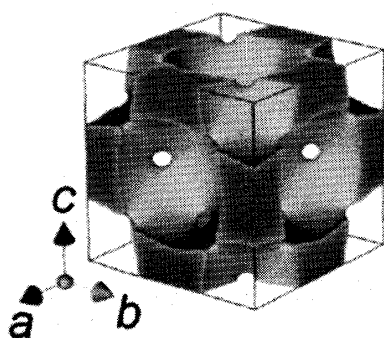


Figure 1. The 3D representation of a unit cell of a calcined silica mesoporous crystal with $Fm\bar{3}m$ symmetry.

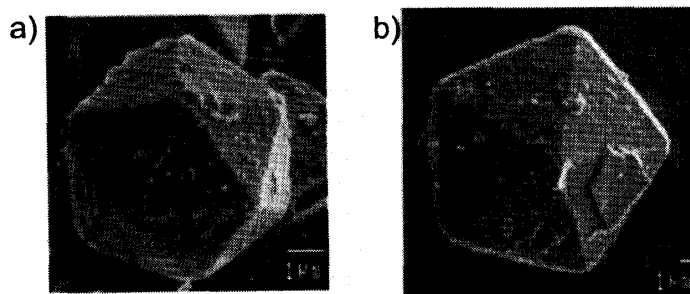


Figure 2. SEM images of a calcined silica mesoporous crystal showing an icosahedron (a) and a decahedron (b).

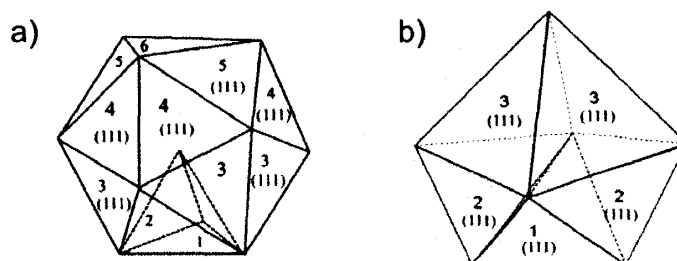


Figure 3. Schematics of MTPs composed of twenty tetrahedral building units for an icosahedron (a) and five tetrahedra for a decahedron (b), where MTPs are surrounded by {111} planes.